

NASA TM-86421

NASA Technical Memorandum 86421

NASA-TM-86421 19850017134

OPTIMIZATION OF THE CATALYTIC OXIDATION OF CO FOR
CLOSED-CYCLE CO₂ LASER APPLICATIONS

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APRIL 1985

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NF00601

INTRODUCTION

High-energy pulsed CO_2 lasers have a potential for measuring many different features of the earth's atmosphere (refs. 1 and 2). For this purpose they are particularly useful on an airborne or space platform. In this application, the laser must be operated closed-cycle to conserve gas, especially if rare chemical isotopes of carbon and oxygen are used. However, the laser discharge decomposes a fraction of the CO_2 to CO and O_2 , which causes a rapid loss in power and leads to erratic behavior. To maintain operation, the CO and O_2 must be recombined to form CO_2 . This conversion can be done by passing the gas mixture over a heated, solid catalyst.

Although many catalysts can oxidize CO to CO_2 , not all are suitable for laser operation because they need an oxidizing atmosphere of about 20% oxygen. This is a large excess of oxygen. However, in the CO_2 laser, the O_2 concentration must be kept below a few tenths of a percent to maintain laser power.

A recent study in this laboratory (ref. 3) has shown that a 1% Pt on SnO_2 (1% Pt/ SnO_2) catalyst tested with a surrogate laser gas mixture of 1% CO and 1/2% O_2 showed considerable removal of CO and O_2 . At 120°C all the CO and 70% of the O_2 were removed. Complete removal of both was observed at 175°C . Subsequently, a closed-cycle CO_2 laser was operated with this catalyst between 120 and 200°C , and laser power was maintained for 6 hours at 93% of full power.

The current study has these goals:

1. To develop a basis for the design of a 1% Pt/ SnO_2 catalyst bed for a closed-cycle CO_2 laser
2. To determine the reaction mechanism of CO and O_2 on the Pt/ SnO_2 catalyst surface
3. To determine whether or not there is isotopic exchange between a rare isotope of oxygen in the gas and bound oxygen in the Pt/ SnO_2 catalyst
4. To optimize the Pt/ SnO_2 catalyst with respect to % Pt.

This report is concerned with progress made in the first and second goals. Succeeding reports will deal with all four goals.

Design Basis for the Catalyst Bed

The purpose of this section is to discuss briefly the design basis for an amount of catalyst that will completely convert CO and O₂ to CO₂ in a closed-cycle CO₂ laser system. The key design parameter is τ , the residence or contact time required for complete conversion of CO to CO₂. This can be defined as

$$\tau = \frac{V_o}{F} \quad (1)$$

where V_o is the void volume of the catalyst and F is the volumetric flow rate of the test gas flowing through the catalyst. V_o can be defined as

$$V_o = V'_o w \quad (2)$$

where V'_o is the specific void volume, or the void volume per unit weight of the catalyst, and w is the weight of catalyst in the bed. V'_o is defined as

$$V'_o = \frac{1}{\rho_b} - \frac{1}{\rho_{\text{SnO}_2}} \quad (3)$$

where ρ_b is the bulk density of catalyst and ρ_{SnO_2} is the literature value for the density of SnO₂. The volume of the 1% Pt relative to the SnO₂ is very small and was neglected.

Equations (1) and (2) can be combined to form a design equation:

$$w = \frac{F\tau}{V'_o} \quad (4)$$

This equation will calculate the weight of catalyst needed for the complete conversion of CO and O₂ for a τ and temperature necessary for this conversion. The specific void volume of the catalyst was determined to be 0.374 cm³/g, therefore,

$$w = \frac{F\tau}{0.374} \quad (5)$$

Experimental

Figure 1 shows a schematic diagram of one of the experimental systems used in our study. This system was used to obtain kinetic data for the reaction of a stoichiometric mixture of CO and O₂ on a 1% Pt/SnO₂ catalyst. The gas mixture, or test gas, was sampled at either the test gas cylinder (the reactor bypass) or at the reactor outlet, as shown in figure 1, and analyzed by a gas chromatograph. The test gas was a mixture of 1% CO and 1/2% O₂ in ultrapure helium, 99.999%. About

0.2% neon was added to this mixture as an internal standard. Moisture in the helium was removed by a silica gel-molecular sieve dryer, while that in the test gas was removed by a magnesium perchlorate dryer.

The chromatographic column was a commercial dual concentric tube column where the outer column, 1.83 m x 0.64 cm, was packed with activated molecular sieve, and the inner column, 1.83 m x 0.32 cm, was packed with a Porapak mixture. The outer column separated the O₂, N₂, and CO from the mixture while the inner column separated the CO₂. A small N₂ peak probably resulted from a small air inleakage. The area of the N₂ peak was used to make a small correction to the area of the O₂ peak. The GC oven temperature was 80°C and helium carrier flow was 43 sccm.

The reactor consisted of a high purity, clear quartz tube 7 mm i.d. by 46 cm long; a 25 cm section of this tube passed through a uniform temperature zone that was controlled at 25°, 55°, 75°, and 100 ± 1°C. The catalyst bed in the reactor weighed 0.925 g and was 1 cm long. It was located in the center of the controlled temperature zone and was confined by a quartz wool plug at each face of the bed.

The catalyst used in the present study was prepared by first oxidizing SnCl₂ (in a solution adjusted to a pH of 7 with Na₂CO₃) with 35% H₂O₂ solution to Sn(OH)₄. The product was filtered, air-dried for 6 to 8 hours at 110°C and pulverized. This powder was impregnated with a concentrated solution of Pt(NH₃)₄(OH)₂. The product was filtered, air-dried for 2 hours at 110°C, then calcined for 5 hours at 450°C in air, followed by grinding to a powder.

At the beginning of a typical run the catalyst bed was purged with helium gas for a minimum of 1 hour at 225°C to remove any adsorbed gases, such as O₂, CO, and CO₂. Then the reactor was cooled with flowing helium gas to one of the four temperatures indicated above. Test gas flow was then initiated through the reactor and adjusted to one of three flows: 5, 10, or 20 sccm. These mass flows were converted to volumetric flows using the temperature and average pressure in the reactor. The neon internal standard in the test gas mixture made it possible to relate the analyses of CO, O₂, and CO₂ to one another independently of the flow rate, pressure or temperature of the sample loop in the GC. At the end of the run, the reactor inlet stream was analyzed.

RESULTS AND DISCUSSION

Figure 2 shows a typical run in which molar ratios of CO₂/Ne, O₂/Ne, and CO/Ne are plotted against elapsed run time in minutes. Initially, the CO₂ concentration decreased while the O₂ and CO concentrations increased. Sometime after 300 minutes, the concentration of these three molecules leveled off, as indicated by the relatively constant value of 4 or more replicates. After this, four replicate analyses of the reactor inlet stream were taken. The conversion of CO and O₂ is based on the average value of each of the two sets of replicates. We define conversion, C, as

$$C = \frac{[B_i] - [B_o]}{[B_i]} \times 100$$

where B_i is the concentration of the reactant at the reactor inlet and B_o is the concentration of the reactant at the reactor outlet.

At a reactor temperature of 100°C, and at a flow rates of 5 and 10 sccm, 100% conversion of both CO and O₂ was observed on a 1% Pt/SnO₂ catalyst weighing 0.925 g. Complete conversion of CO and O₂ was not obtained at 20 sccm. From equation (1), the residence time, τ , for a flow rate of 10 sccm, was calculated to be 1.5 sec. The residence time for 20 sccm was calculated to be 0.75 sec. Thus, the minimum τ for complete conversion is $1.5 > \tau > 0.75$ sec. To be conservative, it will be assumed that $\tau = 1.5$ sec. Based on this value of τ , equation (5) was then used to calculate the weight of catalyst needed for a closed-cycle laser system with a reactor temperature of 100°C and a flow rate of 10,000 sccm.

$$w = \frac{(10,000)(1.5)}{(0.374)(60)}$$

$$= 668 \text{ g.}$$

This quantity of 1% Pt/SnO₂ catalyst, having a Brunauer, Emmett, and Teller (BET)^a surface area of 6.7 m²/g, is the amount of catalyst that should result in an indefinite operation of a closed-cycle CO₂ TEA pulsed laser.

The general rate equation for the reaction of CO and O₂ to form CO₂, is

$$\frac{d[\text{CO}_2]}{dt} = -\frac{2d[\text{O}_2]}{dt} = -\frac{d[\text{CO}]}{dt} = k [\text{CO}]^\alpha [\text{O}_2]^\beta \quad (6)$$

where [CO] and [O₂] are the concentrations of carbon monoxide and oxygen, k is the rate constant, and α and β are the orders of reactant CO and O₂, respectively. An attempt was made to determine the order of the reactant concentrations using a steady state approximation for the oxygen atom concentration.

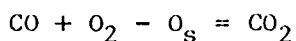
Let us assume that an oxygen molecule dissociates on the catalyst surface to form two oxygen atoms, O_s, or



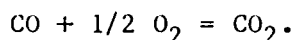
Then an adsorbed or gas phase CO reacts with one of these oxygen atoms to form CO₂, or



Adding these two reactions we get



which is equivalent to the overall reaction



^aThis refers to a method of measuring the real surface area of a solid by nitrogen adsorption (ref. 4)

It follows from (7) that oxygen dissociation is proportional to O_2 concentration:

$$-\frac{d[O_2]}{dt} = k_7[O_2] \quad (9)$$

and from (8) the conversion of CO is proportional to the concentration of O_s and CO.

$$-\frac{d[CO]}{dt} = k_8[O_s][CO] \quad (10)$$

where we assume that the reverse rates for reactions (7) and (8) are negligible. The rate equation for the oxygen atom concentration on the surface may be similarly expressed as

$$\frac{d[O_s]}{dt} = 2k_7[O_2] - k_8[O_s][CO] \quad (11)$$

If we assume a steady state approximation for the oxygen atom concentration, then

$$\frac{d[O_s]}{dt} = 0 \quad (12)$$

Substituting (12) into (11) and solving (11) for $[O_s]$, yields

$$[O_s] = \frac{2k_7[O_2]}{k_8[CO]} \quad (13)$$

Substituting (13) into (10) yields

$$-\frac{d[CO]}{dt} = k_8 \left(\frac{2k_7[O_2]}{k_8[CO]} \right) [CO]$$

which subsequently reduces to

$$-\frac{d[CO]}{dt} = 2k_7[O_2] \quad (14)$$

In our stoichiometric mixture,

$$[O_2] = \frac{1}{2}[CO] \quad (15)$$

Substitution of (15) into (14) yields

$$\frac{d[\text{CO}]}{dt} = -k_7[\text{CO}]. \quad (16)$$

We see that the reaction rate constant, $-k_7$ is the same for O_2 and for $[\text{CO}]$ in the rate equations (9) and (16); the integrated forms of these equations also show this:

$$\ln[\text{O}_2] = -k_7 t + \ln[\text{O}_2]_0 \quad (17)$$

and

$$\ln[\text{CO}] = -k_7 t + \ln[\text{CO}]_0 \quad (18)$$

where $[\text{O}_2]_0$ and $[\text{CO}]_0$ are the initial concentrations of O_2 and CO .

In figure 3, plotted data of $\ln[\text{O}_2]$ versus τ and $\ln[\text{CO}]$ versus τ also show very nearly the same slope, or k_7 , for each temperature of 25°C , 55°C , and 75°C . However, since we have used a stoichiometric gas mixture of CO and O_2 throughout these experiments, the overall order of the reaction is unity (i. e., $\alpha + \beta = 1$), for we could have obtained the same results by assuming zero order in one of the reactants and first order in the other or half order in each. Therefore, other experiments must be run with nonstoichiometric mixtures of CO and O_2 to determine unambiguously the order of each reactant. Once the order is determined the rate law can be established.

CONCLUDING REMARKS

In a surrogate laser system using 0.925 g of a 1% Pt/SnO_2 catalyst (BET surface area of $6.7 \text{ m}^2/\text{g}$) complete conversion of a stoichiometric gas mixture (1% CO , 1/2% O_2 , and the balance He) occurred at 100°C and a flow rate of 10 sccm. From these data, it was determined that a reactor in a closed-cycle CO_2 laser system using 668 g of catalyst at 100°C should operate indefinitely with a circulating gas flow of 10,000 sccm.

An analysis of the kinetic data suggested a rate law for a reaction that is overall first order. However, because a stoichiometric mixture of CO and O_2 was used, it is possible for the reaction to be zero order in either constituent and first order in the other or to be half order in each. Further tests are planned to resolve this problem.

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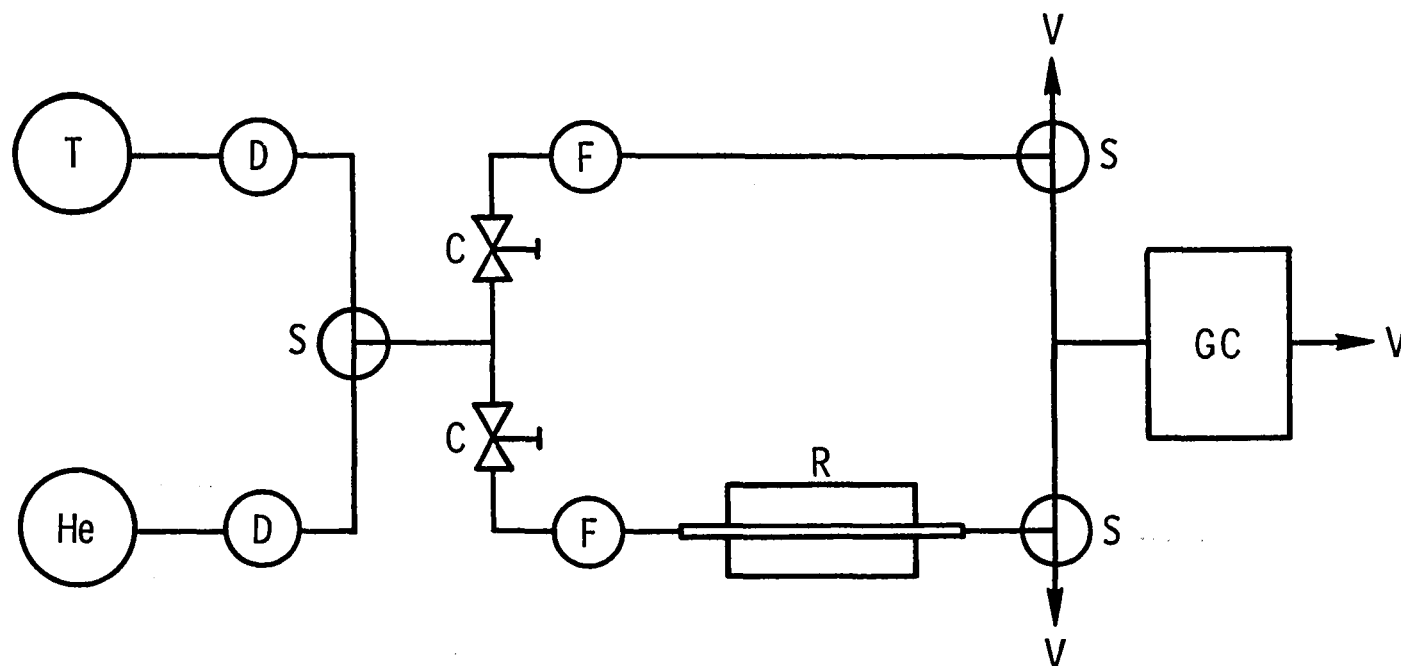


Figure 1. - Schematic diagram of a surrogate laser system for studying the reaction of a stoichiometric gas mixture of 1% CO and 0.5% O₂ in He on a 1% Pt/SnO₂ catalyst. [T - test gas cylinder; He - helium cylinder; D - dryer; S - switching valve; C - control valve; F - flow meter; R - reactor; V - vent; GC - gas chromatograph.]

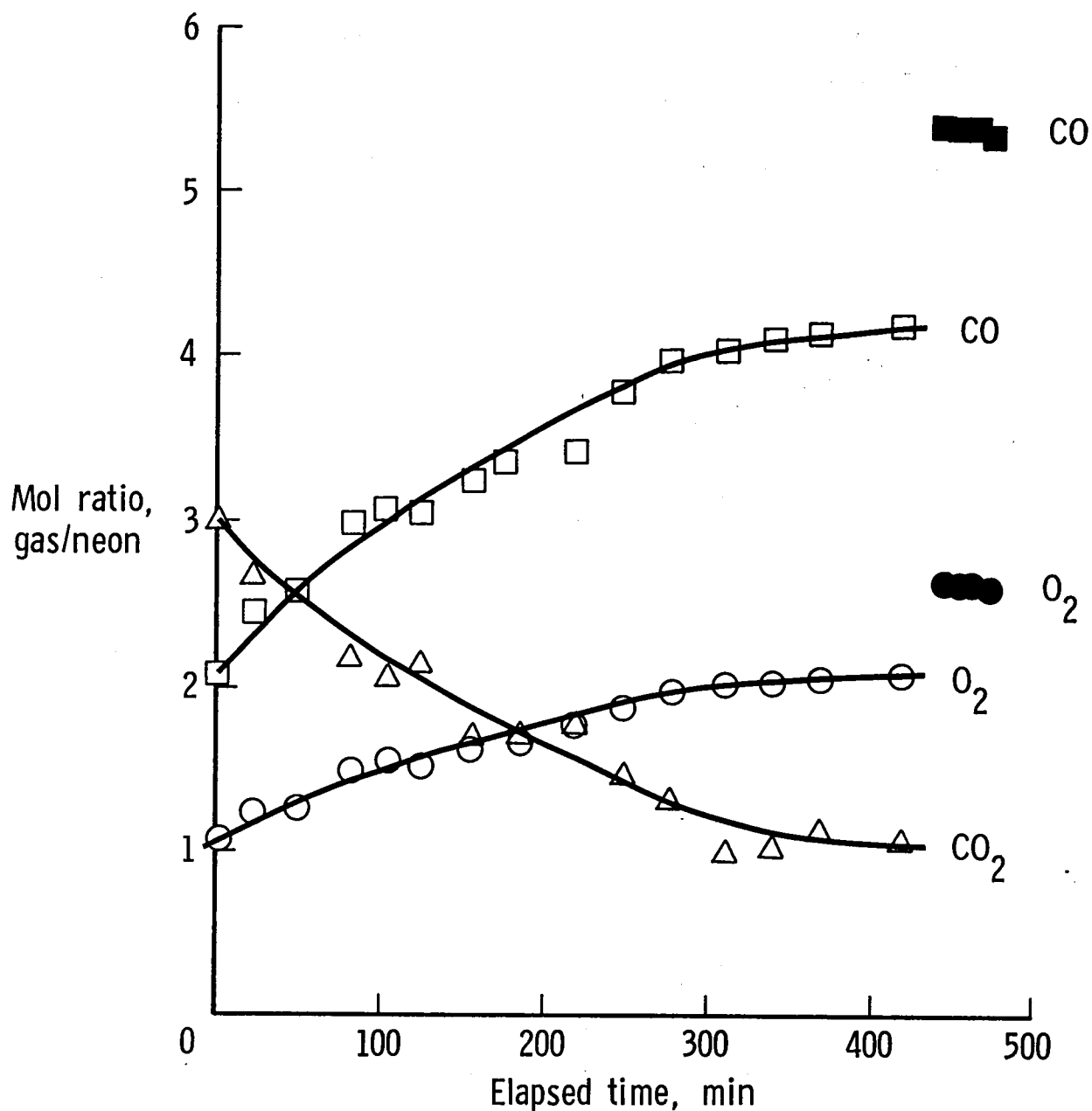


Figure 2. - Time variation of gas/neon concentrations for a reactor temperature of 24°C and a flow rate of 10 sccm. Open symbols are for the reactor outlet; closed symbols are for reactor inlet.

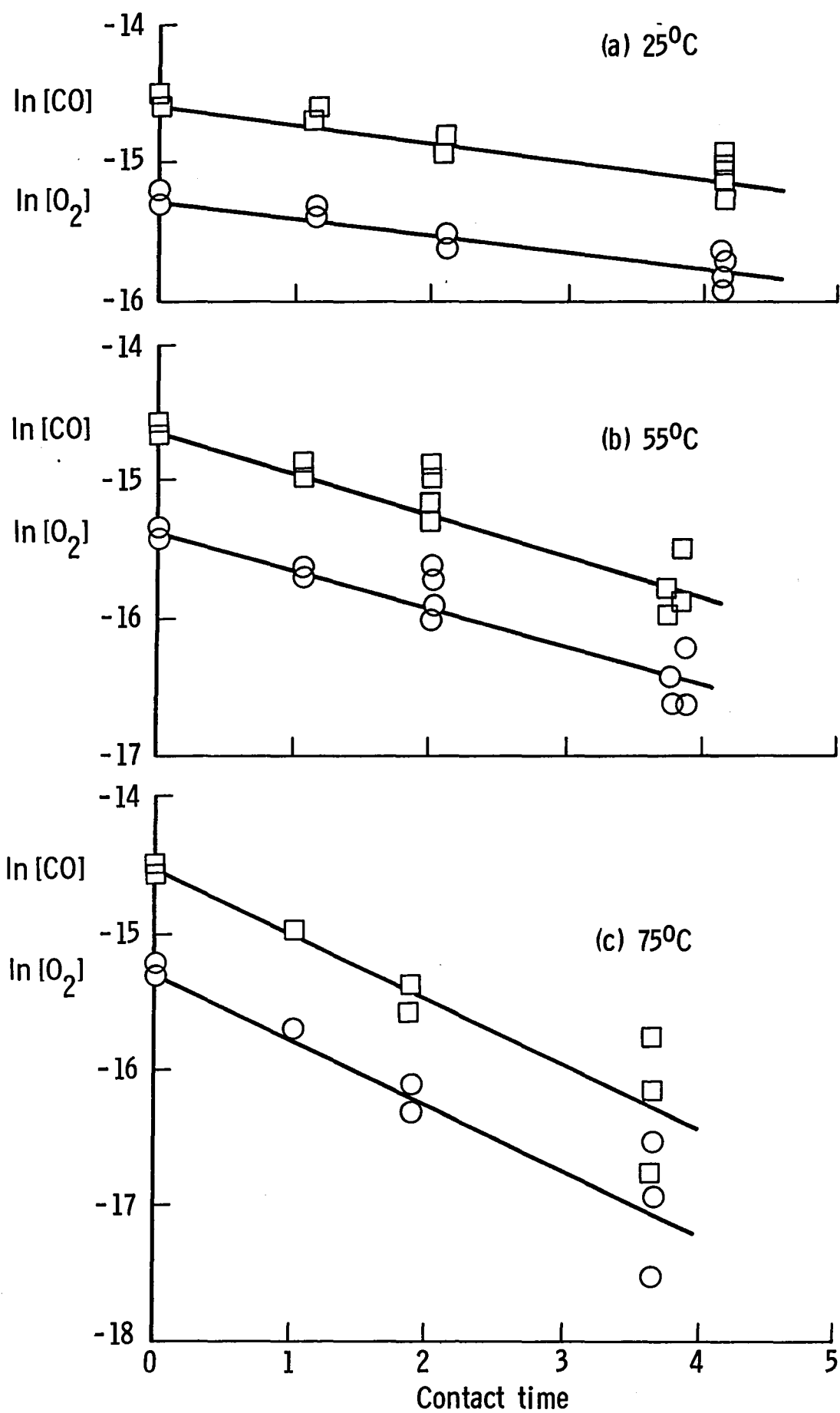


Figure 3. - $\ln [\text{CO}]$ and $\ln [\text{O}_2]$ as a function of contact time.

1. Report No. NASA TM-86421		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Optimization of the Catalytic Oxidation of CO for Closed-Cycle CO ₂ Laser Applications				5. Report Date April 1985	
				6. Performing Organization Code 506-54-23-12	
7. Author(s) I. M. Miller, G. M. Wood, Jr., D. R. Schryer, R. V. Hess, B. T. Upchurch, and K. G. Brown				8. Performing Organization Report No.	
9. Performing Organization Name and Address NASA Langley Research Center Hampton, VA 23665				10. Work Unit No.	
				11. Contract or Grant No.	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546				13. Type of Report and Period Covered Technical Memorandum	
				14. Sponsoring Agency Code	
15. Supplementary Notes I. M. Miller, G. M. Wood, Jr., D. R. Schryer, and R. V. Hess: NASA Langley Research Center, Hampton, Virginia. B. T. Upchurch and K. G. Brown: Old Dominion University, Norfolk, Virginia.					
16. Abstract This report develops a basis for the design of a catalyst bed for the recombination of CO and O ₂ in a closed-cycle CO ₂ laser system. The catalyst is 1% Pt on SnO ₂ having a BET surface area of 6.7 m ² /g and a specific void volume of 0.374 cm ³ /g. The design conditions are: a catalyst bed temperature of 100°C and a circulating flow rate of 10ℓ/min. Under these conditions, the required quantity of catalyst for prolonged laser operation is 668g. The rate law for the reaction of a stoichiometric mixture of 1% CO + 1/2% O ₂ in helium was determined to be overall first order; however, additional experiments with non-stoichiometric gas mixtures of CO and O ₂ are needed to determine the order of the CO concentration and the order of the O ₂ concentration in the rate law.					
17. Key Words (Suggested by Author(s)) CO ₂ laser, 1% Pt/SnO ₂ catalyst, CO oxidation				18. Distribution Statement Unclassified - Unlimited Subject Category 25	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 11	
				22. Price A02	

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